Coherence tendencies in the transport of translationally invariant exciton-phonon systems

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The motion of an exciton in a translationally invariant exciton-phonon system is considered within the frame of the generalized Fulton-Gouterman (FG) transformation, which diagonalizes the coupled exciton-phonon Hamiltonian in the excitonic subspace and yields a set of exact equations for the purely oscillatory FG wave functions. An exact expression for the second moment of the local excitonic occupation numbers is presented in terms of the FG wave functions, for which two different sets of displaced phonon states are discussed. A numerical computation of the second moment characterizes the exciton motion as a coherent process. This result is also found in an improved calculation which is based on the application of the Goldberger-Adams relation. [S0163-1829(96)00137-3]

I. INTRODUCTION

The motion of an exciton in an elastic medium has been intensively studied during the past decades. Various approaches were developed to elucidate the question whether the exciton motion corresponds to a coherent, wavelike propagation or to a diffusive process.[1]

It can be easily shown that a bare exciton, not coupled to other modes, propagates coherently in a translationally invariant chain. A frequently mentioned argument is that, if the exciton is coupled to the phonons in a nondiagonal manner, the interaction between the two subsystems generates scattering processes between various exciton-phonon states and thus gives rise to a transition to a diffusive motion. Expressing this more formally, it means that the nondiagonal part of the coupled exciton-phonon Hamiltonian causes incoherence. It must be objected, however, that unitary transformations alter the definition of what is to be understood as ''diagonal'' and ''nondiagonal'' in the transformed Hamiltonian. Specifically, the scattering terms in the original Hamiltonian may be partially diagonalized by a unitary transformation. Then the question arises whether these diagonal terms, which originally were connected with incoherence, now favor a coherent motion. From these considerations it follows that a transport formalism must be devised, which does not take recourse to semiphenomenological relaxation times for scattering processes, because this approximation possibly leads to results which are artifacts.

In the approach presented here transport quantities are calculated in terms of the wave functions of the model Hamiltonian. At a first glance this appears ineffective due to the large number and the complexity of the involved wave functions. However, this problem is drastically simplified by the application of unitary transformations, by means of which approximative forms for the eigenfunctions of the considered Hamiltonian are constructed. In this context it is essential that unitary transformations conserve orthonormality relations and expectation values.

The dominant mathematical tool of the paper is the generalized Fulton-Gouterman transformation (gFGT),[2,3] which exploits the group-theoretical properties of the model system and diagonalizes the coupled exciton-phonon Hamiltonian with respect to the excitonic subspace. The evolving FG equations are a rigorous substitute for the original Schrödinger equation and they pertain to the phonon subspace only. An exact expression for the second moment of the excitonic occupation probabilities then may be derived, which allows for the characterization of the propagation process. Two sets of approximative solutions for the FG equations are introduced via different unitary displacement operators.[4] The numerical computation of the second moment for both sets of wave functions hints at a coherent exciton motion. These findings are underlined by an improved calculation, which is based on the Goldberger-Adams relation.[5]

In Sec. II the model system is introduced in the frame of the gFGT and an expression for the relevant transport quantity is formulated. Section III contains the description of the applied wave functions and first results. These are confirmed in Sec. IV by improved calculations. In Sec. V the method and the results are summarized and the Appendix describes the calculation of the exact short-time limit.

II. THE GENERALIZED FULTON-GOUTERMAN TRANSFORMATION

A. The model system in the FG picture

We consider the standard model of a Frenkel exciton interacting linearily with acoustic phonons

$$H=\frac{1}{2}\sum_m\left\{\frac{P_m^2}{M}+f(Q_m-Q_{m+1})^2\right\}-T\sum_m\left(|m\rangle\langle m+1|\right.$$

$$\left.+|m+1\rangle\langle m|\right)+D\sum_m\left(Q_{m+1}-Q_{m-1}\right)|m\rangle\langle m|,$$

$$m=0,\pm1,\ldots,\pm\frac{N}{2}. \tag{1}$$

The first term is the acoustic phonon Hamiltonian (molecular force constant f, molecular mass M). The second term describes the bare exciton band of width $4T$ in the Wannier representation, and the third term models the exciton-phonon interaction, which is assumed as local with respect to the

Wannier operators $|m\rangle\langle m|$ and linear in the oscillatory displacements. The pure vibrational Hamiltonian is diagonalized by normal coordinates $\hat{P}_q, \hat{Q}_q$, which are defined by

$$Q_m = (N+1)^{-1/2} \sum_q (M\Omega_q)^{-1/2} \hat{Q}_q e^{+iqm}, \tag{2}$$

$$P_m = (N+1)^{-1/2} \sum_q (M\Omega_q)^{+1/2} \hat{P}_q e^{-iqm}, \tag{3}$$

$$q = n_q \frac{2\pi}{N+1}, \quad n_q = 0, \pm 1, \ldots, \pm \frac{N}{2}. \tag{4}$$

This yields for the Hamiltonian (1)

$$H = \frac{1}{2} \sum_q \Omega_q (\hat{P}_q \hat{P}_{-q} + \hat{Q}_q \hat{Q}_{-q}) - T \sum_m (|m\rangle\langle m+1| + |m+1\rangle\langle m|) + D \sum_{m,q} \Omega_q D_q \hat{Q}_{-q} e^{-iqm} |m\rangle\langle m| \tag{5}$$

with the phonon frequencies Ω_q and the coupling function D_q

$$\Omega_q = \Omega_D \left| \sin\left(\frac{q}{2}\right) \right|, \quad \Omega_D = 2\left(\frac{f}{M}\right)^{1/2}, \tag{6}$$

$$D_q = -2iD \frac{\cos(q/2)}{\sqrt{(N+1) f \Omega_q}} \left| \frac{\sin(q/2)}{\sin(q/2)} \right|,$$

$$D_q = -D_{-q} = -D_q^*. \tag{7}$$

The exact diagonalization of this exciton-phonon Hamiltonian (5) in the excitonic subspace can be performed by means of the generalized Fulton-Gouterman transformation (gFGT), which exploits the translational invariance of the model system. This procedure is described in previous publications,[3,4,6] so that we repeat only the basic formulas in the present paper.

Subjecting Hamiltonian (5) to the gFGT, which is defined by the unitary operator

$$U_{\mathrm{FG}} = (N+1)^{-1/2} \sum_{k,m} e^{ikm} |m\rangle\langle k| R_m^{\mathrm{ph}}, \tag{8}$$

($k = \kappa[2\pi/(N+1)]$, $\kappa = 0, \pm 1, \ldots, \pm N/2$, R_m^{ph}: translational operator in the phonon subspace), yields

$$H_{\mathrm{FG}} = U_{\mathrm{FG}}^{\dagger} H U_{\mathrm{FG}} = \frac{1}{2} \sum_q \Omega_q (\hat{P}_q \hat{P}_{-q} + \hat{Q}_q \hat{Q}_{-q}) + \sum_q \Omega_q D_q \hat{Q}_{-q} - T \sum_k |k\rangle\langle k| (e^{ik} R_1^{\mathrm{ph}} + e^{-ik} R_{-1}^{\mathrm{ph}}), \tag{9}$$

where $\{|k\rangle\}$ denotes the orthonormal basis in the new excitonic subspace. The ansatz $|\Psi_{\mathrm{FG}}^{(k)}\rangle = |k\rangle |\phi^{(k)}(Q)\rangle$ for the eigenfunctions of H_{FG} results in a set of $(N+1)$ oscillatory equations, which are denoted as FG equations,

$$H_{\mathrm{FG}}^{(k)} |\phi_\nu^{(k)}\rangle = \left\{ \frac{1}{2} \sum_q \Omega_q (\hat{P}_q \hat{P}_{-q} + \hat{Q}_q \hat{Q}_{-q}) + \sum_q \Omega_q D_q \hat{Q}_{-q} - T(e^{ik} R_1^{\mathrm{ph}} + e^{-ik} R_{-1}^{\mathrm{ph}}) \right\} |\phi_\nu^{(k)}\rangle = E_\nu^{(k)} |\phi_\nu^{(k)}\rangle. \tag{10}$$

The form of the wave functions in the original, i.e., combined Hilbert space reads

$$|\Psi_\nu^{(k)}\rangle = U_{\mathrm{FG}} |(\Psi_{\mathrm{FG}}^{(k)})_\nu\rangle = (N+1)^{-1/2} \sum_m e^{ikm} |m\rangle R_m^{\mathrm{ph}} |\phi_\nu^{(k)}\rangle. \tag{11}$$

Having introduced the gFGT, which establishes the mathematical framework for our treatment, we now turn to questions regarding the dynamical behavior of the model system.

B. Transport calculations in the FG frame

We assume that at time $t=0$ the phonon subsystem is in a uniform equilibrium state, described by $\rho_{\mathrm{ph}}(t=0) = \rho_{\mathrm{ph}}$ and an exciton is created instantaneously at site $m=0$ (excitonic state $|0\rangle$). Thus the initial exciton-phonon density matrix reads

$$\rho(t=0) = |0\rangle\langle 0| \otimes \rho_{\mathrm{ph}}. \tag{12}$$

In the course of the temporal evolution of this initial local excitation the lattice will be distorted and the exciton will be delocalized. The primary aim of the present paper is to examine whether the exciton propagation is of a coherent or a diffusive nature. This question can be clarified by calculating the local occupation numbers

$$n_m(t) = \mathrm{Tr}\{|m\rangle\langle m| \rho(t)\}, \tag{13}$$

which measure the probability of finding the exciton at site m, irrespective of the state of the phonons. We define the moments of the excitonic distribution $n_m(t)$,

$$M_r(t) = \sum_m m^r n_m(t). \tag{14}$$

We are especially interested in the time dependence of the second moment $M_2(t)$, because it characterizes the specific type of the propagation process. Coherent processes are connected with a t^2 long-time limit of $M_2(t)$,

$$\lim_{t\to\infty} M_2^{\mathrm{coh}}(t) \propto t^2, \tag{15}$$

whereas a diffusive propagation pertains to a linear increase of $M_2(t)$,

$$\lim_{t\to\infty} M_2^{\mathrm{dif}}(t) \propto t. \tag{16}$$

For the calculation of $M_2(t)$ we start with the Liouville equation

$$i\frac{d\rho}{dt}=\mathcal{L}\rho, \tag{17}$$

where $\mathcal{L}$ denotes the Liouville superoperator, $\mathcal{L}A=[H,A]$. Equation (17) is formally solved by

$$\rho(t)=e^{-i\mathcal{L}t}\rho(0)=e^{-iHt}\rho(0)e^{iHt}. \tag{18}$$

With this form the local occupation numbers $n_m(t)$ of Eq. (13) are given by

$$n_m(t)=\sum_{k,\nu}\langle k\nu|[|m\rangle\langle m|e^{-i\mathcal{L}t}\rho(0)]|k\nu\rangle, \tag{19}$$

where $\{|k\nu\rangle\}$ is an arbitrary complete orthonormal base. If we identify the base $\{|k\nu\rangle\}$ with the eigenbase $\{|\Psi_\nu^{(k)}\rangle\}$, as defined by Eq. (11), the matrix elements in the excitonic subspace can be evaluated and $n_m(t)$ is expressed in terms of the solutions $|\phi_\nu^{(k)}\rangle$ of the FG equations via

$$n_m(t)=(N+1)^{-2}\sum_{k,\nu}\sum_{k',\nu'}\underbrace{\exp[-i(k-k')m]}_{m\ \text{dependent}}\exp[i(E_\nu^{(k)}-E_{\nu'}^{(k')})t]\underbrace{\langle\phi_\nu^{(k)}|\phi_{\nu'}^{(k')}\rangle}_{\neq\delta_{k,k'}\delta_{\nu,\nu'}}\langle\phi_{\nu'}^{(k')}|\rho_{ph}|\phi_\nu^{(k)}\rangle. \tag{20}$$

It is important to note that the scalar product $\langle\phi_\nu^{(k)}|\phi_{\nu'}^{(k')}\rangle$ is not equal to $\langle\phi_\nu^{(k)}|\phi_{\nu'}^{(k')}\rangle=\delta_{k,k'}\delta_{\nu,\nu'}$, because the FG functions pertaining to two different irreducible representations k and k' are eigenfunctions of two different FG Hamiltonians, $H_{\mathrm{FG}}^{(k)}$ and $H_{\mathrm{FG}}^{(k')}$, and therefore they are not necessarily orthogonal to each other. As a second important feature of the right-hand side (rhs) of Eq. (20), we note that it contains only one factor, which depends on the site index m.

From this presentation of $n_m(t)$ the moment of zeroth order $M_0(t)$ is easily derived,

$$M_0(t)=\sum_m n_m(t)=(N+1)^{-1}\sum_{k,\nu}\langle\phi_\nu^{(k)}|\rho_{\mathrm{ph}}|\phi_\nu^{(k)}\rangle=1. \tag{21}$$

This corresponds to the conservation of the exciton number. For the formulation of $M_2(t)$ in terms of the FG functions $|\phi_\nu^{(k)}\rangle$ we apply the relation

$$\sum_{m=-N/2}^{N/2}m^2e^{-i(k-k')m}=\delta_{k,k'}\frac{N(N+1)(N+2)}{12}+(1-\delta_{k,k'})\frac{N+1}{2}(-1)^{\kappa-\kappa'}\times\frac{\cos[(k-k')/2]}{\sin^2[(k-k')/2]}, \tag{22}$$

$(k=\kappa[2\pi/(N+1)]$, κ integer), and with the initial condition $M_2(t=0)=0$ we arrive at the final expression

$$M_2(t)=-(N+1)^{-1}\sum_{\substack{k,k'\\(k\neq k')}}\sum_{\nu,\nu'}f_{k-k'}\langle\phi_\nu^{(k)}|\phi_{\nu'}^{(k')}\rangle\langle\phi_{\nu'}^{(k')}|\rho_{\mathrm{ph}}|\phi_\nu^{(k)}\rangle\sin^2\left(\frac{E_\nu^{(k)}-E_{\nu'}^{(k')}}{2}t\right), \tag{23}$$

where

$$f_{k-k'}=(-1)^{\kappa-\kappa'}\frac{\cos[(k-k')/2]}{\sin^2[(k-k')/2]}. \tag{24}$$

This formulation of the second moment $M_2(t)$ is exact and the knowledge of the complete set of the solutions $|\phi_\nu^{(k)}\rangle$ of the FG equations (10) would allow for the accurate characterization of the excitonic energy transfer. The FG equations, however, in general cannot be solved exactly and therefore approximative forms of the phononic wave functions $|\phi_\nu^{(k)}\rangle$ must be considered.

For the calculations of the following sections we consider the initial phonon density matrix

$$\rho_{\mathrm{ph}}=|\varphi_0\rangle\langle\varphi_0|, \tag{25}$$

which means that at the moment of the creation of the exciton the lattice is in its ground state $|\varphi_0\rangle$. It would be possible to examine other initial conditions, such as a partially

dressed exciton[7] or the case of thermal equilibrium at a finite temperature,[8] but in this paper we want to discuss only the simple version of Eq. (25).

III. CONSTRUCTION OF THE WAVE FUNCTIONS

A. General method

In this section we construct approximative forms of the FG wave functions. Our general philosophy will be as follows. We relate the choice of $|\phi_\nu^{(k)}\rangle$ to unitary transformations, i.e., we define these functions by the application of a unitary operator $U^{(k)}$, which may depend on the irreducible representation k, onto a given orthonormal set $\{|\varphi_\nu\rangle\}$ of simple functions,

$$|\phi_\nu^{(k)}\rangle = U^{(k)}|\varphi_\nu\rangle. \tag{26}$$

The state vectors $|\varphi_\nu\rangle$ are assumed to be the eigenfunctions of the uncoupled phonon Hamiltonian

$$H_0 = \frac{1}{2}\sum_q \Omega_q(\hat{P}_q\hat{P}_{-q} + \hat{Q}_q\hat{Q}_{-q}). \tag{27}$$

The unitary operator $U^{(k)}$ may contain adjustable parameters which can be optimized by means of a suitable variational principle. This procedure has the advantage that the orthonormality between the FG functions $|\phi_\nu^{(k)}\rangle$ is warranted as a consequence of the orthonormality between the phonon states $|\varphi_\nu\rangle$.[9]

In the present paper we restrict our considerations to the case of an excitonic band that has a smaller energetic width than the phonon band, i.e, $4T<\Omega_D$. In this parameter regime the FG functions are adequately described by displaced phonon states,[4,10] which can be generated by the application of the unitary displacement operator $U_{\rm dis}$ onto the pure phonon states $|\varphi_\nu\rangle$. Thus we choose for $U^{(k)}$

$$U^{(k)} \equiv U_{\rm dis}(\{d_q^{(k)}\}) = \exp\left(i\sum_q d_q^{(k)}\hat{P}_q \right). \tag{28}$$

If we transcribe the displacement transformation into the original, not the FG transformed picture, it corresponds to the the well-known polaron[11] or Lang-Firsov transformation.[12] In a space where the excitonic coordinates are considered as continuous and not as discrete ones as in the present work, the transformation connected with $U_{\rm dis}$ is identified as second Lee-Low-Pines (LLP) transformation.[13] In this context it should also be noted that there exists a close relationship between the first LLP transformation and the gFGT.[14]

From the transformation prescriptions

$$T_{\rm dis}:\hat{Q}_q = U_{\rm dis}^\dagger\hat{Q}_q U_{\rm dis} = \hat{Q}_q - d_q^{(k)}, \tag{29}$$

$$T_{\rm dis}:\hat{P}_q = U_{\rm dis}^\dagger\hat{P}_q U_{\rm dis} = \hat{P}_q, \tag{30}$$

it follows that $d_q^{(k)}$ is the $\hat{Q}$-space displacement of mode q. In the further proceeding we will discuss two different forms for the parameters $\{d_q^{(k)}\}$.

B. Simple choice for the mode displacements

The first choice for $d_q^{(k)}$ is

$$d_q^{(k)} \equiv D_q. \tag{31}$$

The unitary transformation defined by $\exp(i\Sigma_q D_q\hat{P}_q)$ exactly diagonalizes the FG Hamiltonian of Eq. (10) in the limit of a vanishing excitonic band width, $T=0$, and it may be considered as a first step towards the explicit calculation of the second moment $M_2(t)$.

The ansatz (31) means that the displacements $\{d_q^{(k)}\}$ and consequently the operators $U^{(k)}$ are identical for all k values, $U^{(k)}=U$. Thus the wave functions $|\phi_\nu^{(k)}\rangle$ are given by

$$|\phi_\nu^{(k)}\rangle \equiv |\phi_\nu\rangle = U|\varphi_\nu\rangle = \exp\left(i\sum_q D_q\hat{P}_q \right)|\varphi_\nu\rangle, \tag{32}$$

irrespective of the irreducible representation k. For this case $M_2(t)$ assumes the simplified form

$$M_2(t) = -(N+1)^{-1}\sum_{k,k'}{}'\sum_\nu f_{k-k'}\langle\varphi_\nu|U^\dagger\rho_{\rm ph}U|\varphi_\nu\rangle \times \sin^2\left(\frac{E_\nu^{(k)} - E_\nu^{(k')}}{2}t\right), \tag{33}$$

where the energy eigenvalue $E_\nu^{(k)}$ is approximated by the energy expectation value $E_\nu^{(k)} = \langle\phi_\nu|H_{\rm FG}^{(k)}|\phi_\nu\rangle$.

C. Alternative choice

Besides the simple form Eq. (31) we also examine a more complicated alternative for $d_q^{(k)}$. If the ansatz

$$|\phi_0^{(k)}\rangle = \exp\left(i\sum_q d_q^{(k)}\hat{P}_q \right)|\varphi_0\rangle, \quad |\varphi_0\rangle: \text{phonon vacuum state}, \tag{34}$$

is employed as a trial wave function for the ground-state solution of the FG equations (10) an energy minimization procedure yields a set of self-consistency equations for the mode displacements $d_q^{(k)}$,[6,15]

$$d_q^{(k)} = \frac{D_q}{1 + 4(T/\Omega_D)L_1(\{d_q^{(k)}\})\cos k|\sin(q/2)|} \tag{35}$$

with the Debye-Waller factor

$$L_1(\{d_q^{(k)}\}) = \langle\varphi_0|U_{\rm dis}^\dagger R_{\pm 1}U_{\rm dis}|\varphi_0\rangle = \exp\left[-\sum_q \left| d_q^{(k)} \right|^2 \sin^2\left(\frac{q}{2}\right) \right] \tag{36}$$

as an integral quantity for the complete set $(\{d_q^{(k)}\})$. Replacing $(4T/\Omega_D)L_1\cos k$ in Eq. (35) by a variational parameter $\lambda^{(k)}$ the coefficients $d_q^{(k)}$ are given by

$$d_q^{(k)}(\lambda^{(k)}) = \frac{D_q}{1+\lambda^{(k)}|\sin(q/2)|} \tag{37}$$

and $\lambda^{(k)}$ is determined by optimizing the energy expression

$$E_0^{(k)}(\lambda^{(k)}) = -2TL_1 \cos k - \frac{D^2}{f}(4\Gamma_1 - 2\Gamma_2) \tag{38}$$

with the sum quantities

$$L_1(\lambda^{(k)}) = \exp\left(-\frac{4D^2}{f\Omega_D}\frac{1}{N+1}\sum_q \frac{\cos^2(q/2)|\sin(q/2)|}{[1+\lambda^{(k)}|\sin(q/2)|]^2}\right), \tag{39}$$

$$\Gamma_m(\lambda^{(k)}) = \frac{1}{N+1}\sum_q \frac{\cos^2(q/2)}{[1+\lambda^{(k)}|\sin(q/2)|]^m}. \tag{40}$$

The approximative forms for the FG functions read

$$|\phi_\nu^{(k)}\rangle \equiv U_{\rm dis}(\lambda^{(k)})|\varphi_\nu\rangle = \exp\left(i\sum_q d_q^{(k)}(\lambda^{(k)})\hat{P}_q\right)|\varphi_\nu\rangle \tag{41}$$

with $d_q^{(k)}(\lambda^{(k)})$ defined in Eq. (37).

D. First results

For the numerical computation of $M_2(t)$ we only take into account those contributions in $\langle\phi_\nu^{(k)}|\phi_{\nu'}^{(k')}\rangle\langle\phi_{\nu'}^{(k')}|\rho_{ph}|\phi_\nu^{(k)}\rangle$ [see Eq. (23)], which are of zeroth to second order in the coupling constant D. With this restriction it turns out that for $|\varphi_\nu\rangle$ in Eq. (33) or (41), respectively, we only need to consider the phonon vacuum and the one-phonon states, which in terms of the generating operators $b_q^\dagger = 2^{-1/2}(\hat{Q}_q^\dagger - iP_q)$ are presented by

$$|\varphi_\nu\rangle = \begin{cases} |\varphi_0\rangle \\ b_q^\dagger|\varphi_0\rangle \end{cases} \tag{42}$$

$$\text{with } q = n_q[2\pi/(N+1)].$$
$$n_q = 0, \pm 1, \ldots, \pm N/2.$$

In Fig. 1 the results pertaining to the two different sets of FG functions are illustrated for the coupling strength $D^2/(f\Omega_D) = 0.04$ and the bandwidth ratio $4T/\Omega_D = 0.8$ depending on scaled time τ, which is defined via

$$\tau = 2Tt. \tag{43}$$

For lucidity we do not show the second moment $M_2(\tau)$ itself, but the second derivative of $M_2(\tau)$ with respect to the scaled time τ,

$$\frac{1}{2}\frac{d^2M_2(\tau)}{d\tau^2}. \tag{44}$$

In order to estimate the quality of the approximative results the curve for the exact short-time limit Eq. (59) (see the Appendix) is also sketched (long-dashed curve). The simple choice Eq. (32) for the FG functions $|\phi_\nu^{(k)}\rangle$ results in a finite constant for $(1/2)(d^2M_2/d\tau^2)$ (short-dashed line), what corresponds to $M_2 \propto \tau^2$. The comparison with the exact limiting behavior for small τ reveals that the ansatz Eq. (32) is a crude approximation. It does not reproduce the finite time the lattice needs to react upon the excitonic excitation.

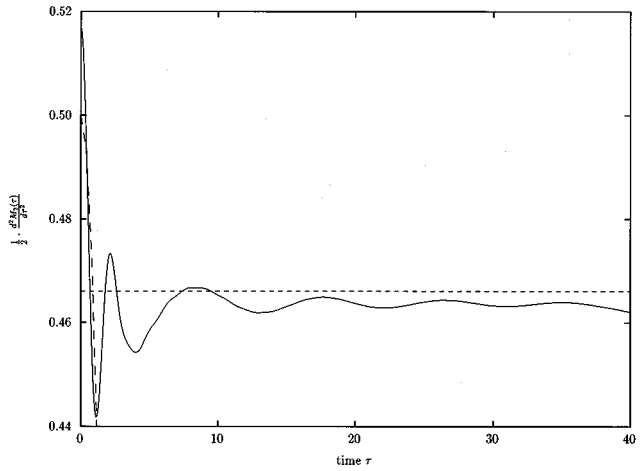

FIG. 1. Temporal evolution of the second derivative of $M_2(t)$ with respect to the time τ. Chain length $N+1=101$ lattice sites, coupling strength $D^2/(f\Omega_D)=0.04$, bandwidth ratio $4T/\Omega_D=0.8$. Exact short-time limit from Eq. (59) (long dashes), simple choice Eq. (31) for mode displacements (short dashes), and improved choice Eq. (37) (solid line).

Regarding this point the alternative choice of Sec. III C for $|\phi_\nu^{(k)}\rangle$ yields an improved description. It displays a qualitatively correct behavior in the short-time limit although the quantitative values differ from the exact ones (e.g., ≈ 0.52 versus 0.50 for $\tau=0$). For larger τ the k-dependent displacement transformation of Eq. (41) generates a curve which asymptotically approaches a finite constant <0.5. (For $\tau>35$ effects due to the finite extension of the fundamental periodicity interval make their appearance.) Thus both approximative forms Eqs. (32) and (41) for the solutions of the FG equations (10) indicate a coherent exciton propagation with a velocity which is smaller than that for the motion of an uncoupled exciton.

Naturally the question arises, whether these findings are artifacts of our approximations or whether they reflect actual system properties. The confidence of the results in the long-time limit certainly would be increased if we found a method which allows for an accurate reproduction of the second moment for small τ. This is presented in the next section.

IV. IMPROVEMENT VIA GOLDBERGER-ADAMS RELATION

A. Introduction of the Goldberger-Adams relation

The preceding considerations were based on the attempt to find suitable approximative solutions $|\phi_\nu^{(k)}\rangle$ of the FG equations. As one possibility to improve the calculations one could search for further unitary transformations, e.g., squeezing transformations,[16] which yield an improved diagonalization of the FG Hamiltonian. It is illuminating, however, to follow up also an alternative path.

Given a complete and orthonormal set of base functions $\{|k\nu\rangle\}$, which are not necessarily eigenfunctions of the considered Hamiltonian, H can be presented in the projective form

$$H=\underbrace{\sum_k \sum_\nu |k\nu\rangle\langle k\nu|H|k\nu\rangle\langle k\nu|}_{H_{\text{diagonal}}}+\underbrace{\sum_k \sum_{\substack{\nu,\nu' \\ \nu\neq\nu'}} |k\nu'\rangle\langle k\nu'|H|k\nu\rangle\langle k\nu|}_{H_{\text{nondiagonal}}}. \tag{45}$$

Similarly, the Liouvillian $\mathcal{L}$, appearing in the basic expression (19), may be written in a projective form. Writing

$$\mathcal{L}=\mathcal{L}_d+\mathcal{L}_{nd} \tag{46}$$

we have

$$\mathcal{L}_d A=[H_d,A]$$
$$=\sum_k \sum_\nu \langle k\nu|H|k\nu\rangle(|k\nu\rangle\langle k\nu|A-A|k\nu\rangle\langle k\nu|), \tag{47}$$

$$\mathcal{L}_{nd} A=[H_{nd},A]$$
$$=\sum_k \sum_{\substack{\nu,\nu' \\ \nu\neq\nu'}} \langle k\nu'|H|k\nu\rangle(|k\nu'\rangle\langle k\nu|A-A|k\nu'\rangle\langle k\nu|), \tag{48}$$

and we may introduce the Goldberger-Adams (GA) transcription[5]

$$e^{-i\mathcal{L}t}=e^{-i\mathcal{L}_d t}+\int_0^t dt' e^{-i\mathcal{L}_d(t-t')}(-i\mathcal{L}_{nd})e^{-i\mathcal{L}t'}. \tag{49}$$

We start again with expression (19), but rather than employing the exact eigenbase $\{|\Psi_\nu^{(k)}\rangle\}$ for $\{|k\nu\rangle\}$ we allow the latter to be different and make use of the GA transcription. In this transcription the time evolution of the density matrix $\rho(t)$ reads

$$\rho(t)=e^{-i\mathcal{L}t}\rho(0)=e^{-i\mathcal{L}_d t}\rho(0)$$
$$-i\int_0^t dt' e^{-i\mathcal{L}_d(t-t')}\mathcal{L}_{nd}e^{-i\mathcal{L}_d t'}\rho(0)$$
$$-\int_0^t dt'\int_0^{t'} dt'' e^{-i\mathcal{L}_d(t-t')}\mathcal{L}_{nd}e^{-i\mathcal{L}_d(t'-t'')}$$
$$\times\mathcal{L}_{nd}e^{-i\mathcal{L}_d t''}\rho(0), \tag{50}$$

where the series expansion of the GA relation has been applied up to second order in $\mathcal{L}_{nd}$. This expression now is used in Eq. (19),

$$n_m(t)=\sum_{k,\nu}\langle k\nu|(|m\rangle\langle m|e^{-i\mathcal{L}_d t}\rho(0))|k\nu\rangle-i\sum_{k,\nu}\langle k\nu|(|m\rangle\langle m|\int_0^t dt' e^{-i\mathcal{L}_d(t-t')}\mathcal{L}_{nd}e^{-i\mathcal{L}_d t'}\rho(0))|k\nu\rangle$$
$$-\sum_{k,\nu}\langle k\nu|(|m\rangle\langle m|\int_0^t dt'\int_0^{t'} dt'' e^{-i\mathcal{L}_d(t-t')}\mathcal{L}_{nd}e^{-i\mathcal{L}_d(t'-t'')}\mathcal{L}_{nd}e^{-i\mathcal{L}_d t''}\rho(0))|k\nu\rangle. \tag{51}$$

The second moment $M_2(t)$ [vid. Eq. (14)] now is calculated by choosing

$$|k\nu\rangle=(N+1)^{-1/2}\sum_m e^{ikm}|m\rangle R_m^{\text{ph}}|\hat{\phi}_\nu^{(k)}\rangle, \tag{52}$$

where $\{|\hat{\phi}_\nu^{(k)}\rangle\}$ is a complete orthonormal set of approximate eigenfunctions of the FG equations. Specifically, for $|\hat{\phi}_\nu^{(k)}\rangle$ we make two particular choices. On the one hand we use for $|\hat{\phi}_\nu^{(k)}\rangle$ Eq. (32), on the other hand, Eq. (41).

If this is done, the present approach amounts to an improvement of the calculation in the preceding sections. This improvement is achieved via the second and third terms on the rhs of Eq. (50). The calculation in the preceding sections can be viewed as one in which only the first term of Eq. (50) is employed. We refrain from writing down the respective expressions for the second moments, since they are lengthy but straightforward.

B. Improved results

Figure 2 contains the results which are calculated via the extended expression (50) for the time-dependent density matrix $\rho(t)$. Analogously to Fig. 1 the quantity $(1/2)[d^2M_2(\tau)/d\tau^2]$ is presented for the simple ansatz Eq. (32) (short-dashed line) and for the alternative set of wave functions established by Eq. (41) (solid line). For small τ both curves practically coincide with the exact short-time limit (long-dashed line, see the Appendix). For intermediate τ, $5<\tau<25$, both lines display a qualitatively similar behavior with small quantitative differences. For large times the two curves asymptotically approach a finite constant, which within the given accuracy is identical for both sets of approximative FG solutions. As from Fig. 1 we draw the conclusion that the exciton propagation corresponds to a coherent process with a velocity which is reduced by the interaction with the acoustic lattice vibrations. The coincidence of the results pertaining to different sets of wave func-

tions both in the short-time limit as well as for large τ reduces the probability that our findings are artifacts of the formalism.

V. SUMMARY

In the present paper we have developed a formalism for the calculation of transport quantities within the frame of the gFGT. It offers the advantage that no semiphenomenological concepts such as relaxation times for scattering processes must be introduced. Moreover there is no need for a separation of the considered degrees of freedom into relevant and irrelevant sets, as in the approaches via generalized Master equations. Therefore our formalism is easily extended from the calculation of excitonic expectation values as presented here to the determination of quantities which pertain to the oscillatory subsystem.

As a first application we have derived an exact expression for the second moment of the local excitonic occupation numbers in terms of the solutions of the FG equations. Two different sets of approximative FG functions were established by the application of different unitary displacement operators onto the eigenstates of the uncoupled phonon Hamiltonian. With these base functions indications were found that for periods of time, in which the wings of the excitonic distribution do not reach the border of the model system, the excitonic propagation can be considered as a coherent process. These findings are confirmed by transient grating experiments of Burland *et al.*,[17] who observed that exciton transport in pure crystals at low temperatures can be wavelike. Following the aforementioned argument the coherence time in physical systems can be estimated by dividing the sample extension by the velocity of sound which results in a coherence time of the order of microseconds. This estimation is justified if one assumes the excitonic and the phononic bandwidths of the same order of magnitude.

In the present paper we treat a closed system with a finite number of degrees of freedom. It might be objected that for such a model the dynamics is coherent due to a finite recovery time. A glance at Figs. 1 and 2, however, reveals that the presented curves display no periodic behavior. Furthermore, the recovery time for a system with 202 degrees of freedom, as in our case, is remarkably larger than the evolution times considered here. From that we conclude that our treatment is also valid for an infinitely extended model.

In conclusion we want to emphasize what we consider to be the main outcome of the present investigation. In most preceding theories of exciton transport the phonon subsystem is considered as a kind of bath, which somehow causes the excitonic propagation to become diffusive. Our main goal has been to clarify whether this is true under the provision of *strict translational invariance*. In our approximation we find that there is no excitonic diffusivity under the assumed symmetry prerequisite, if the temperature is zero. Since our calculation reproduces the exact short-time limit and is stable in the long-time limit, our finding may seem to be a strong indication that diffusive behavior must be due to other interaction processes (defects, etc.) than those inherent in a strictly translationally invariant exciton-phonon coupling Hamiltonian.

For further theoretical studies it appears especially interesting whether a transition to a diffusive propagation is found if the influences of finite temperature and lattice defects are included in the calculations. By this means the source of finite diffusion constants in doped crystals[18–21] could be investigated without introducing incoherence *a priori* by the application of effective transport equations or phenomenological damping parameters. Moreover the energy propagation within the phonon degrees of freedom can be treated, which may be relevant with regards to the possible existence of solitary modes in the considered coupled exciton-phonon model.

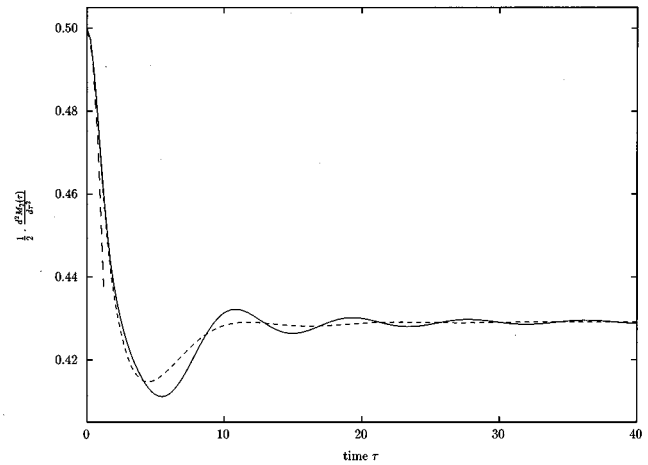

FIG. 2. Temporal evolution of the second derivative of $M_2(t)$ with respect to the time τ, corrected via the Goldberger-Adams relation Eq. (49). Chain length $N+1=101$ lattice sites, coupling strength $D^2/(f\Omega_D)=0.04$, bandwidth ratio $4T/\Omega_D=0.8$. Exact short-time limit (long dashes), simple choice Eq. (31) for mode displacements (short dashes), and improved choice Eq. (37) (solid line).

APPENDIX: EXACT SHORT-TIME LIMIT

In order to estimate the quality of the results obtained with the FG formalism we derive an exact expression for the short-time expansion of $M_2(t)$ in the original, not FG transformed frame. In the Schrödinger picture this can be achieved by the expansion of the time-dependent density matrix given in Eq. (18),

$$\rho(t)=e^{-i\mathcal{L}t}\rho(0)$$
$$=\rho(0)-it[H,\rho(0)]-\tfrac{1}{2}\,t^2[H,[H,\rho(0)]]\cdots \tag{A1}$$

with the initial condition

$$\rho(0)=|m=0\rangle\langle m=0|_{\mathrm{ex}}\otimes|\varphi_0\rangle\langle\varphi_0|_{\mathrm{ph}}. \tag{A2}$$

The second moment $M_2(t)$ then reads

$$M_2(t)=\sum_m m^2\{\mathrm{Tr}(|m\rangle\langle m|\otimes\rho(0))$$

$$-it\ \mathrm{Tr}(|m\rangle\langle m|\otimes[H,\rho(0)]) \tag{A3}$$

$$-\tfrac{1}{2}\ t^2\ \mathrm{Tr}(|m\rangle\langle m|\otimes[H,[H,\rho(0)]])\cdots\}. \tag{A4}$$

Alternatively one can change to the Heisenberg representation where $M_2(t)$ amounts to

$$M_2(t)=\sum_m m^2\{\mathrm{Tr}(\rho(0)\otimes|m\rangle\langle m|)$$

$$+it\ \mathrm{Tr}(\rho(0)\otimes[H,|m\rangle\langle m|]) \tag{A5}$$

$$+\tfrac{1}{2}\ t^2\ \mathrm{Tr}(\rho(0)\otimes[H,[H,|m\rangle\langle m|]])\cdots\}. \tag{A6}$$

This form is more suitable for the determination of $M_2(t)$, because it is easier to calculate the commutator of the exciton-phonon Hamiltonian (1) with the pure exciton operator $|m\rangle\langle m|$ than with the exciton-phonon density operator $\rho(0)$ of Eq. (A2).

The exact short-time limit for $N>5$ amounts to

$$M_2(\tau)=\frac{1}{2}\ \tau^2-\frac{1}{45\pi}\ \frac{D^2}{f\Omega_D}\ \frac{\Omega_D^2}{T^2}\ \tau^4+\mathcal{O}(\tau^6). \tag{A7}$$

In the limit of a vanishing coupling $D=0$ the second moment increases quadratically in time and the propagation process is completely coherent. For finite D the exciton transfer is modified due to the interaction with the lattice. The short-time limit, however, offers no possibility to determine whether the propagation process is coherent or diffusive, or to calculate, e.g., diffusion coefficients, because these quantities are related with the long-time behavior of the excitonic motion.

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